

2004 DOE HYDROGEN, FUEL CELLS, AND INFRASTRUCTURE
TECHNOLOGIES PROGRAM REVIEW MEETING

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**Novel Approach to
Non-Precious Metal Catalysts**

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This presentation does not contain any proprietary or confidential information

Project Objectives

Overall:

- Demonstrate & develop non-precious metal **NPM cathode catalyst**
 - to **lower cost (50 % less vs. target of 0.2 g Pt/peak kW)**
 - to **reduce the dependence** of PEM fuel cell catalysts **on precious metals**
- Additionally, **identify opportunities** for
 - **system cost reduction**, through breakthroughs in key area of the fuel cell, the catalyst
 - application of **cost-effective processes for MEA fabrication**, closely associated with the development of the new catalyst

Sept. 2003 – May 2004:

- Investigate **Fe-N-C as a model** catalytic site
- Test **1- and 2- step synthesis** processes
- **Fabricate** & characterize **MEA's** from initial NPM samples

Budget

(\$ in millions)

	Total	DOE	Contractor
Total	3.61	2.89	0.72
FY04	1.00	0.80	0.20

Technical Barriers and Targets

- DOE Technical Barriers for Fuel Cell Components
 - O. Stack Material and Manufacturing Cost
 - P. Durability
 - Q. Electrode Performance
- Technical Targets
 - **Performance comparable to platinum** used in current MEAs at a **cost 50% less** compared to a target of **0.2 g Pt/peak kW**
 - **Durability** of greater than **2000 hours** with less than 10% power degradation

Approach

To develop new, **vacuum deposited**, NPM catalysts, 3M is utilizing:

- 3M's infrastructure for, and understanding of, catalysts generated by previous and concurrent 3M/DOE cooperative agreements
 - High TM/low Pt catalysts
 - 3M's unique nanostructured thin film substrate
 - Processes compatible with high volume manufacturability
- Recent insights regarding non-Pt based ORR catalysts for PEMFC's
 - Published work regarding ORR catalysts, e.g. Fe-N-C moieties identified by Dodelet (see, e.g., *J. Phys. Chem. B*, 104(2000)11238) (Designated as "**model catalyst**" in this presentation)
 - Advances and knowledge regarding vacuum deposited precursors suitable for forming TM catalysts, including a variety of carbon based materials

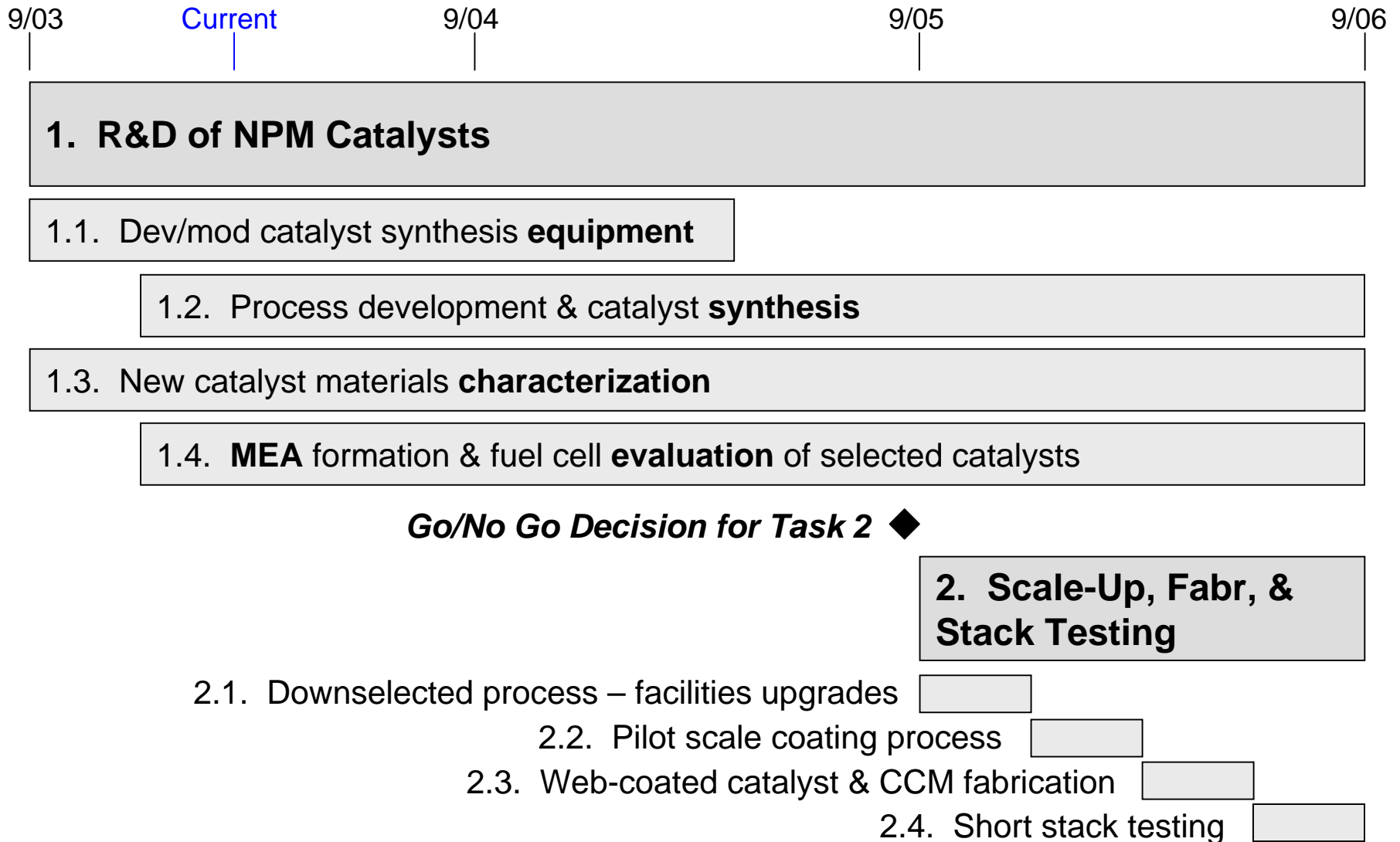
Safety

3M's established procedures regarding safety-related issues include

- Hazard Reviews to ensure compliance with environmental, health, and safety requirements. Required for
 - New or modified facilities, equipment, & processes
 - Fabrication & testing equipment
 - Laboratory & Manufacturing
- New Product Introduction system
 - Risk assessment process in the design and production of products
 - Life Cycle Management process
 - Change Management

No unusual safety issues have been encountered to-date on this project.

Project Timeline



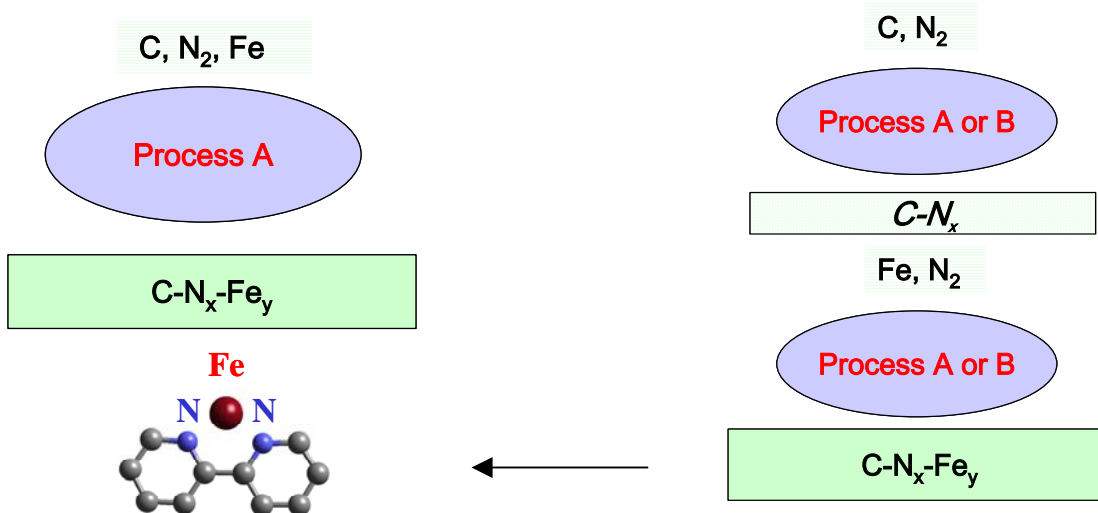
Project Accomplishments

In the initial phase, **reproducing Fe – N – C as a model** catalytic site was attempted. In that regard, we have:

- Produced **highly nitrogenated carbon** by processes compatible with high volume production, mostly in **pyridinic** form.
- Demonstrated **one-step synthesis process** for producing the targeted chemical structure.
- **Formed & characterized 50-cm² MEA's** from the new catalyst.
- **Modeled** the incorporation of nitrogen and iron in the graphene layers.

Synthesis & Characterization of NPM Catalyst

Fabricated catalyst materials by 1- and 2-step processes.



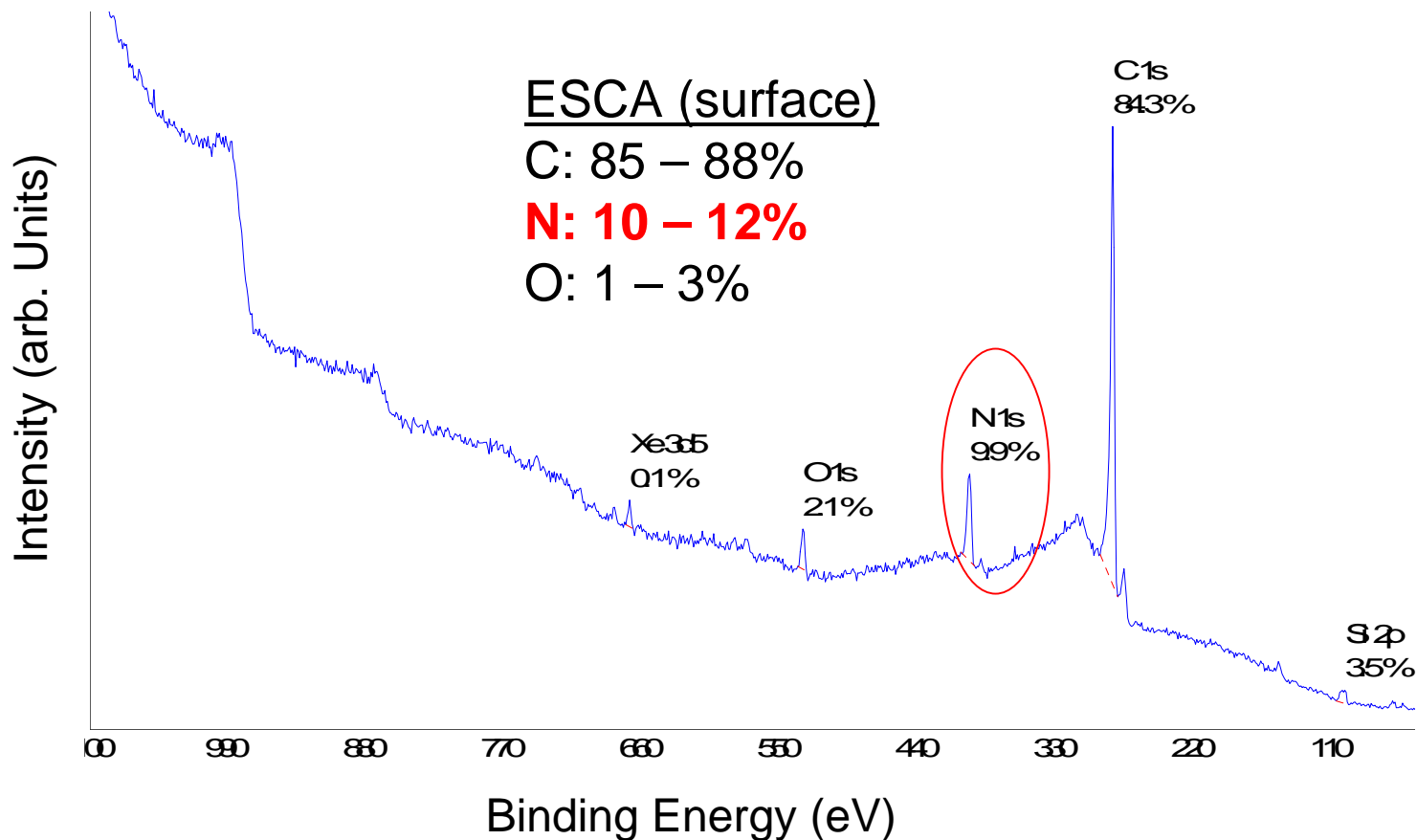
Conducted physicochemical and electrochemical characterization.

- Materials Fabricated
 - 43 substrate coatings (12 carbon, 28 C-N_x)
 - 13 C-N_x-Fe_y catalyst materials via Process A, one-step synthesis
 - 30 TM catalyst synthesis via Process B, two-step
- Physicochemical Characterization
 - ESCA analysis on 43 samples, 140 spectra
 - XRF: 28 samples, 39 spectra
- Electrochemical Characterization
 - over 50 fuel cells

C-N_x Precursor: Nitrogen Content

High nitrogen content necessary, but not sufficient, for high surface density catalyst sites.

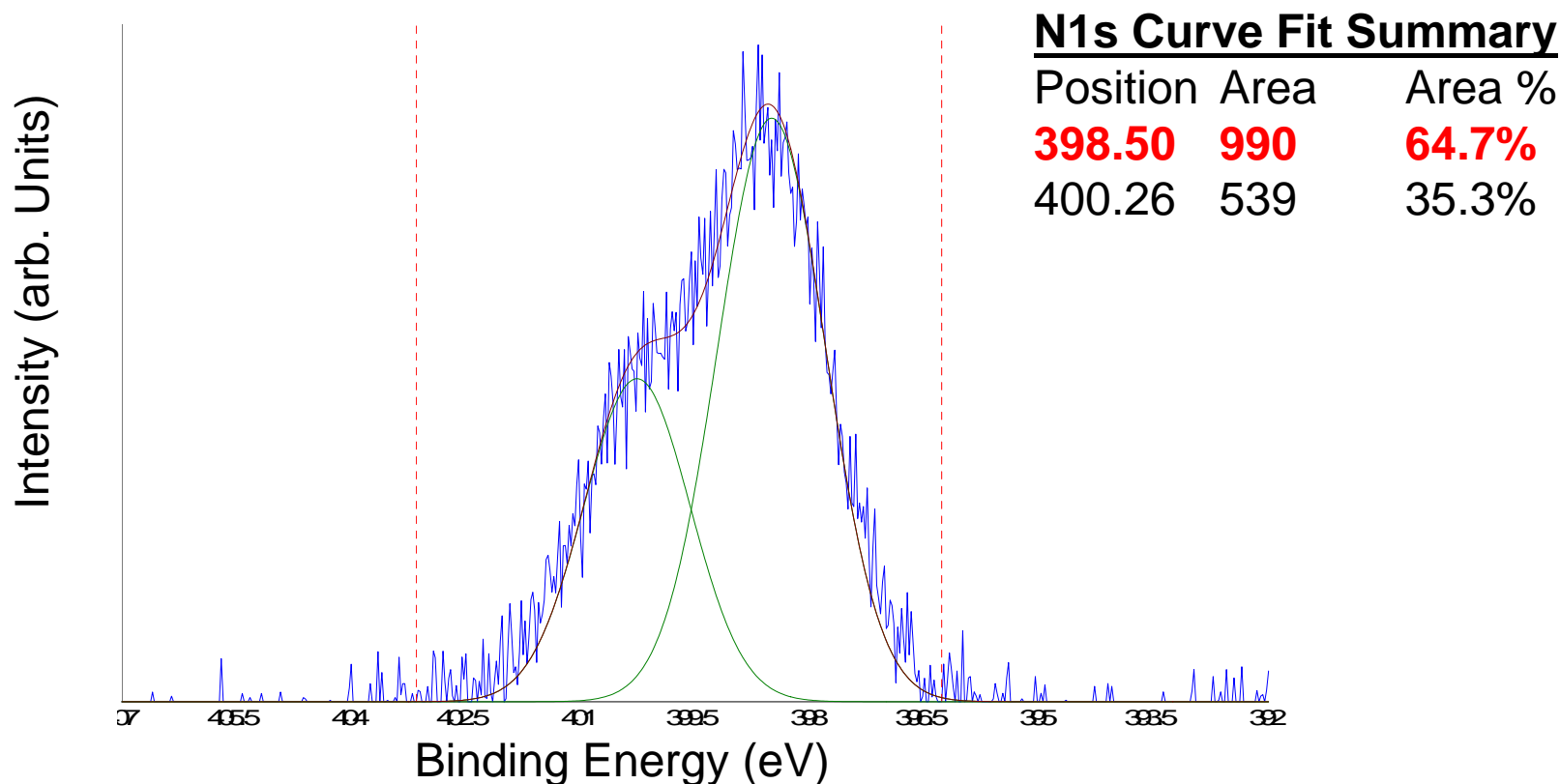
- Achieved **5 times higher N content** than in the model catalyst.



Percentage of Pyridinic Nitrogen in Fe-N-C

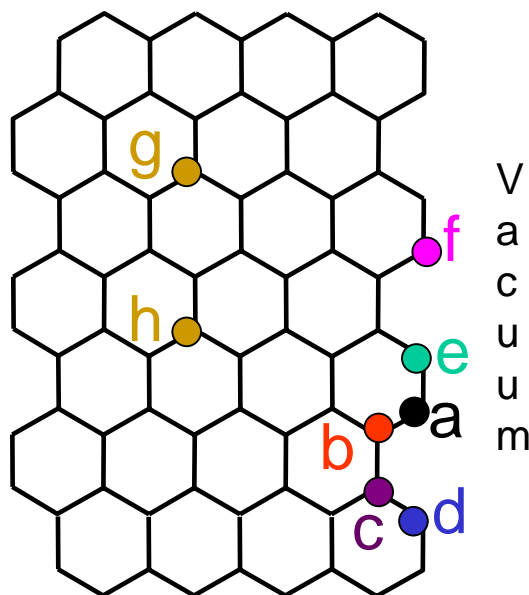
To form high catalytic activity sites, nitrogen must be in pyridinic form.

- Achieved **15 – 20 % higher pyridinic N** than in model catalyst.



Modeling: Nitrogen on Graphite Edge

Heat of formation from the reaction: $\text{N}_2 + \text{C}_x \rightarrow \text{C}_{(x-2)}\text{N}_2 + 2\text{C}_{(\text{graphite})}$



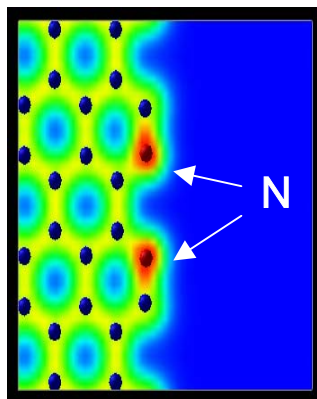
Positions of N atoms	Heat of substitution (eV)	Relative Energy (eV)
a-b	-2.89	0.0
a-c	-3.26	-0.37
a-d (model)	-4.78	-1.89
a-e	-4.65	-1.76
a-f	-4.78	-1.89
g-h (bulk)	1.55	---

- Substituting carbon for nitrogen in the graphene edges is thermodynamically favorable, especially if two N atoms are far apart.
- Substitution in the bulk is unfavorable.

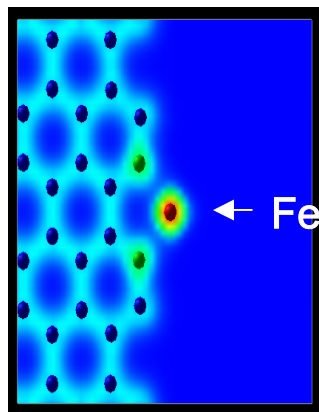
Model Catalyst Calculations: Fe-N₂-C

Electron charge distribution

Incorporation of **2 N atoms in pyridinic sites** on the edge of a graphene sheet (upper).

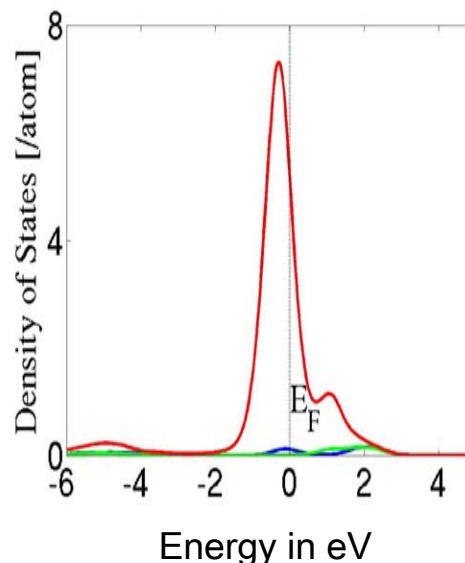


Iron appears to **be in Fe²⁺** and injects charge into the support (lower).



1. VASP (Vienna Ab-initio Simulation Package)
2. Plane waves for electron wavefunction.
3. Projector Augmented Waves (PAW)
4. PBE exchange correlation functional

Partial **Fe-d** Density of States

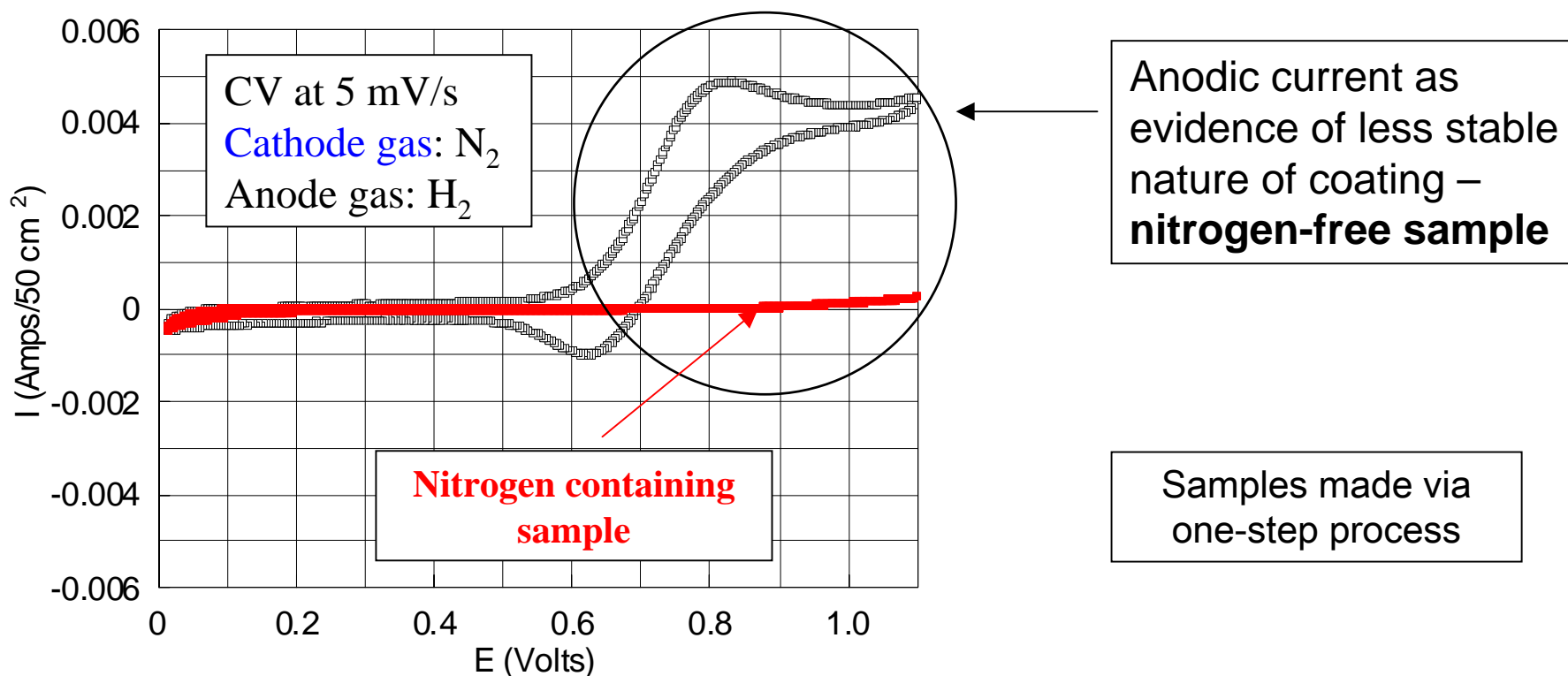


Fe-d states are close to Fermi level and may be **available for catalytic activity**.

Electrochemical Characterization: Stability Evaluation

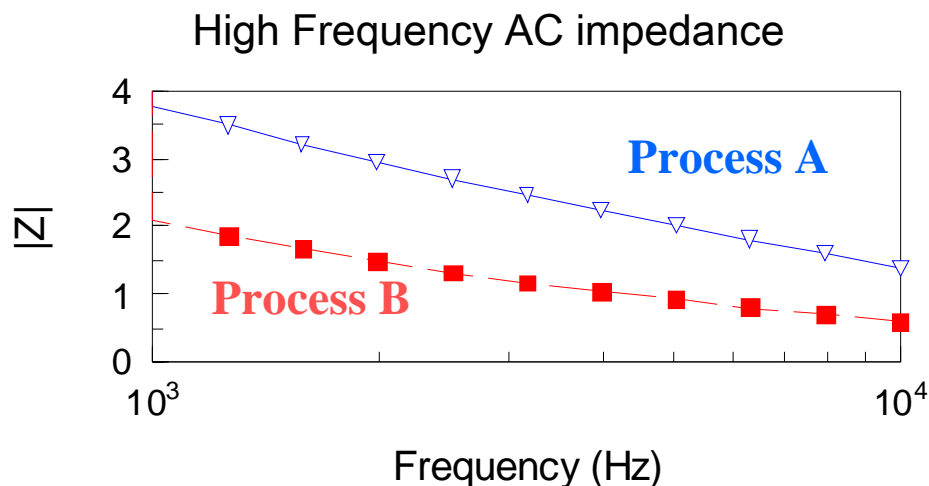
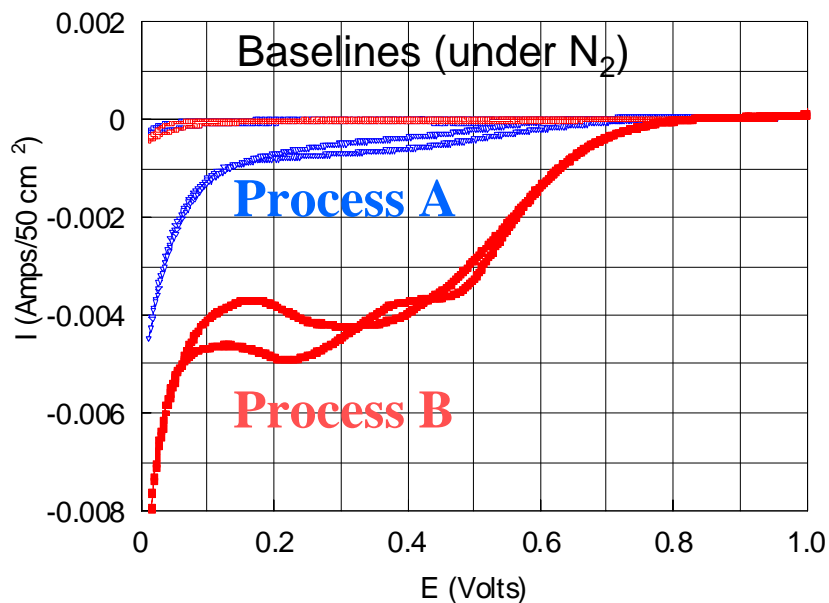
Comparison of samples made **with** and **without** nitrogen

- CV's indicate **films made with nitrogen are more stable**.



Electrochemical Characterization: Oxygen Response

Comparison of samples made by **one-step** (Process A) or by depositing TM on nitrogenated carbon from (Process B)



- TM coated on N-C exhibits better activity and lower impedance than one-step sample without losing stability.
- All the building blocks for the model catalyst are in place, but electrochemical activity remains to be improved.

Future Plans

- Assess appropriateness of nitrogenated carbon precursor for transformation into catalyst.
 - Thermal application of TM to achieve TM – N – C model catalyst
- Identify the nature of the most active sites.
 - Intensify and expand the use of physicochemical methods (XPS, XRF, etc.).
- Continue modeling leading to promising NPMC systems.
- Explore boundaries of the NPMC space.
 - Broaden the range of process variations and key synthesis parameters.
 - Use of fast screening methods (subcontract with Jeff Dahn)